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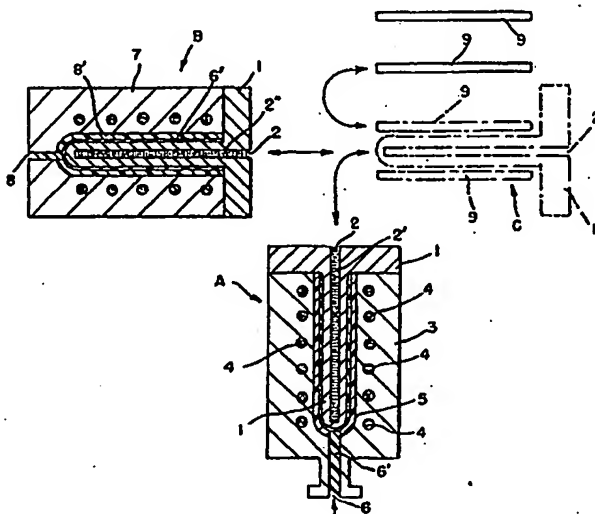
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(54) Title: HOLLOW CONTAINERS HAVING A VERY THIN INERT OR IMPERMEABLE INNER SURFACE LAYER BY COATING THE INSIDE SURFACE OF THE PREFORM



(57) Abstract

A very thin inner layer (6') composed of a polymer chosen for its barrier and/or inertness properties is fabricated within a container preform (8', 14) constructed mainly from another polymer, or a structure of polymers. The inner layer (6') on the preform is produced either by a controlled coating method involving coating of the injection mold core rod (1) prior to injection molding or by a coating applied directly to the preform (14) after injection molding. This enables both inner and main layers to be brought together at a time, when the interface between them is molten. A tie layer can be employed, when desirable, to enable the layers to be combined without melting the layer interface.

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HOLLOW CONTAINERS HAVING A VERY THIN INERT  
OR IMPERMEABLE INNER SURFACE LAYER BY  
COATING THE INSIDE SURFACE OF THE PREFORM

BACKGROUND OF THE INVENTION

This invention relates to hollow containers with inert and/or impermeable inner surfaces and, more particularly, to such containers produced by the application of a thin coating either directly to the container preform or to the core rods of the preform injection machine.

Plastic containers have been replacing glass in many applications where easy handling, low weight and non-breakability are needed. To date, polymers have had varying degrees of inertness to the packaged content which differ from the inertness of glass. In the case of plastic food packages, surface inertness helps diminish potential desorption of packaging material components into the food, to prevent flavor absorption, to avoid loss of food constituents through the package walls and to avoid ingress of air or other substances from outside the package.

Refillable plastic packages add a further dimension to inertness requirements because these packages must withstand washing and refilling. Such containers should not absorb contact materials including, inter alia, washing agents and materials stored in the container.

Packages for carbonated beverages are pressurized and must withstand considerable mechanical stress in handling. It is therefore difficult for a single material to provide the necessary mechanical stability and the required inertness.

Current plastic packages for carbonated beverages consist of either a single material, e.g. polyethylene

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terephthalate (PET), or of multi-layer structures where the middle layers normally provide the barrier properties while the outer layers provide the required mechanical strength.

5 Multi-layer containers are produced either by coinjection or coextrusion but these processes restrict choice of materials and cannot provide a very thin inner layer.

10 Therefore, a plastic container with an impermeable, dense, "glass-like" inner surface cannot be produced by conventional methods because these limit the options for the internal surface. Where a plastic, such as high-crystalline PET has good barrier properties but poor transparency, a very thin inner  
15 layer is needed so that the transparency of the container as a whole is not impaired. Where a plastic, intended as inner layer, has a different glass transition temperature than the main container material, it cannot be blow-molded unless the inner  
20 layer is very thin and can be subjected to individual heat treatment. And, where a barrier plastic has residual monomers or depolymerization by-products, such as acetaldehyde for PET, these can be extracted or deaerated from a very thin layer but not from a  
25 thick layer. Accordingly, more polymer options are possible with very thin layer structures.

30 Recycling is yet another dimension insofar as mass-produced packages are concerned. The reuse of recycled plastic for same purpose, that is to produce new containers ("closed-loop" recycling) is an issue which has attracted much attention, and for PET, this has been achieved to-date by depolymerizing the recycled material in order to free it of all trace  
35 contaminants which might otherwise migrate and come in contact with the container content. An impermeable inner layer, which is the purpose of this invention,

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would enable recycled material to be reused directly for new containers i.e. without special treatment such as depolymerization, since traces of foreign substances could no longer contact the container's content. This would simplify the "closed-loop" recycling process considerably by obviating the need for depolymerization.

Furthermore, recyclability within established recycling systems, both "open-loop", i.e. recycling for other uses, or "closed-loop", i.e. reuse for same purpose, is necessary for any mass-produced package. In "open-loop" systems, the normal method is to separate, clean and chop up the plastic into small flakes. The flake is then either melted and used for molding other objects, or for fibre production. For this form of recycling, it is important to note that any contaminant to the main plastic, such as a coating, should effectively be present in negligible quantities and, preferably, be solid and insoluble within the molten plastic so that it can be filtered off prior to sensitive applications, such as fibre-production. PET is also recycled in "closed-loop" by depolymerization and it is important that the coating material should be unchanged by this process, be insoluble in the monomers resulting from the process, and be easily separable from these monomers. With a correct choice of material, a thin, inner layer can fulfill these criteria.

Finally, since one option available when using a single very thin layer is to use a highly crystalline version of the same polymer as is used in the main part of the container, e.g. highly crystalline PET in PET containers, the inner layer is virtually the same as the outer and recycling presents no problems.

As a result of these inherent limitations, current technology cannot now produce containers with

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a high barrier inert inner layer having a good appearance because it forces compromises which detract from the desired end result which is an improved beverage container.

5

#### SUMMARY OF THE INVENTION

Accordingly, it is the primary object of this invention to fabricate a very thin inner layer composed of a polymer chosen for its barrier and/or inertness properties within a container constructed mainly from another polymer, or same polymer in a significantly more crystalline state, or a structure of polymers.

This and other objects are fulfilled by a method and apparatus for forming a thin inner polymer layer within the preform, then further reducing the thickness of this layer when the container is subsequently formed by stretch blowing. The inner layer on the preform is produced either by a controlled coating method involving coating of the injection mold core rod prior to injection molding or by a coating applied directly to the reheated surface of the preform after injection molding. This enables both inner and main layers to be brought together at a time when the interface between them is molten. Such fabrication offers resistance to subsequent delamination. Additionally, this enables one to use a conventional tie layer, if necessary, and also enables the layers to be combined, where appropriate, without melting the layer interface. Furthermore, this enables use of an inner layer whose glass transition temperature is different from that of the main material in the preform.

Since a very thin layer of polymer is used, the problems of residual monomers, or other extractables, can be resolved by conventional means, such as by deaeration or extraction which is at present far less

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practicable when the material layer used is thicker, or when the material in contact with the food does not present a good barrier to migration from other layers within the container wall structure. Finally, since  
5 some barrier materials have poor transparency, the use of a very thin layer enables transparency problems to be avoided or at least reduced. This invention therefore provides greater flexibility in selecting the material for the inner contact layer of a  
10 container on the basis of its barrier properties and inertness, thereby avoiding undesirable compromises which are imposed by the current technology.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully  
15 understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of illustration only, and thus, are not limitative of the present invention and wherein:

Figure 1 is a diagrammatic view of a method in  
20 accordance with a first embodiment of the present invention;

Figure 2 is a diagrammatic view of an alternative method in accordance with a second embodiment of the present invention;

25 Figure 3 is a cross sectional view of Figure 2 taken along the lines 3-3 thereof;

Figures 4A-4C are cross sectional views illustrative of a third method of the present invention; and

30 Figure 5 is illustrative of the pre-stretch blowing reheating apparatus used in connection with the present invention, whenever differential heating is required for the inner layer.

#### DETAILED DESCRIPTION OF THE INVENTION

35 Referring now to the drawings and more particularly to Figure 1, shown thereat is a preferred

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method in accordance with this invention for providing injection molding core rods with a coating of a molten barrier material as an added function of a conventional injection molding machine.

5       According to Figure 1, a conventional injection molding core rod 1 is first heated internally at A by passing a heating fluid 2' into the channel 2. A core rod receiver 3 has a plurality of channels 4 and an inner lining 5 of a high temperature, low adhesion polymer, such as polytetrafluoroethylene (PTFE). A  
10       heating fluid 4' flows in channels 4. The core rod 1 first enters into the core rod receiver 3. This leaves a small gap between core rod 1 and core rod receiver 3 which is made to reflect the coating thickness required for the core rod. Molten polymer  
15       is next fed into an entrance port 6 and fills the gap between the core rod 1 and the core rod receiver 3.

      The core rod 1 then exits the core rod receiver 3 with a predetermined coating thickness of molten  
20       barrier material 6' and enters the conventional injection cavity mold 7 at B. The flow of heating fluid 2' in channel 2 is then interrupted and a cooling fluid 2'' is introduced. The main container molding material 8' is then injected through entry  
25       port 8 and flows over the molten barrier material to form a preform with a very thin inner layer comprised of the barrier material 6'.

      An alternative to the process described above is to use the core rod receiver 3 at A as a conventional  
30       injection mold. In this case, the core rod 1 is first cooled by applying cooling fluid 2'' to channel 2 and the core rod receiver 3 is cooled by cooling fluid, not shown, in the channels 4. The core rod 1 then enters into the core rod receiver 3 and molten barrier  
35       material 6' is injected through the entrance port 6, filling the gap between core rod 1 and core rod



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receiver 3. The material in the gap solidifies and core rod 1 withdraws from core rod receiver 3 taking the solidified barrier material 6' as an external sleeve since this adheres to core rod 1 rather than to the inner lining 5.

A heating element 9 is next positioned around the core rod 1 as shown by the phantom lines at C to melt the external skin of the barrier material 6' coating sleeve on core rod 1. The heating element 9 then swings out of the way of core rod 1 which then enters injection cavity mold 7 at B and the main molding material 8' is injected through port 8 to produce the finished preform in the manner described.

If the adhesion between the barrier material 6' used in the inner layer of the preform and the main material 8' of the preform require an adhesive or "tie-layer", which materials are conventionally available for many applications, it can be introduced by using another receiver, not shown, identical to the core rod receiver 3 in parallel therewith. The adhesive material is injected into this additional receiver and the core rod 1, after being coated with either a molten layer of barrier material 6' or with a solid layer 8' in a manner already described, is introduced into the additional receiver so as to receive a coat of adhesive prior to entering injection mold cavity 7 shown at B.

Finally, if an interface adhesive is used, the heating of the sleeve formed around the core rod 1 by heater 9 at C can be avoided depending on adhesive and polymers used.

The process thus described can, when desired, be applied to an injection molding machine having a plurality of core rods 1 and cavity molds 7 by providing a core rod receiver 3 with a plurality of cavities and, if necessary, a plurality of core rod

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receivers for adhesive.

Figure 2 is illustrative of another method for applying a coating 6' to the core rod 1. As shown, a depositor 10 includes an inner channel 11 and a depositing slot 12. Molten barrier material 6' is fed into port 13 where it flows to a depositing slot 12 as shown in Figure 3. The depositor 10 can then be swung into position as shown at A and rotated to apply an even coating of molten barrier material 6' around the core rod 1. The internal channel 2 of core rod 1 is supplied with heating fluid 2' to maintain the coating around core rod 1 in a molten state.

The depositor 10 then swings out of the way as shown at B and the core rod 1 enters the injection cavity mold 7 as shown at C where the main molding material, not shown, is injected to produce a finished preform as before.

The depositing slot 12 (Figure 3) can be adjustable if required to provide an even, controlled layer of deposition on the core rod 1.

If the adhesion between the barrier material 6' used in the inner layer of the preform and the main material 8' of the preform requires an adhesive, not shown, it would be introduced by using a second and identical depositor 10, also not shown. After deposition of the barrier material on the core rod 1, the depositor 10 then swings out of the way and an identical, second depositor, supplied with the adhesive, deposits the adhesive layer prior to the core rod 1 entering the injection molding cavity 7 at C.

This process can be implemented, when desirable, with a multiplicity of core rods 1 and cavity molds 7 by providing a plurality of depositors 10 and, if necessary, a plurality of identical depositors for adhesive.

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Although not shown, an alternative to coating the core-rod 1 by using a depositor of the type indicated by Fig. 2 is to coat the inside of the preform 14 (Fig. 4) using a depositing device as in Fig. 2 by dimensionally adapted to enter the preform 14 cavity.

5 Considering now Figure 4A, disclosed thereat is a method for applying a thin coating of barrier material 6' directly using a container preform 14. As shown at A, the container preform 14 is inserted into  
10 a cooling mantel 20 equipped with cooling channels 21. A radiant heater 15 melts the inner surface of the preform 14 while the main body of the preform 14 is kept cool. At B, the preform 14 is withdrawn from the cooling mantel 20 and a depositor 16 injects an  
15 appropriate, accurately metered amount of molten barrier material 6'. At C, a displacement rod 18 having an elongated central channel 19 first enters the preform 14 and displaces the molten barrier material 6' so that it is evenly spread inside the  
20 preform 14. If necessary, during this phase, a heating fluid, not shown, can be made to flow in the channel 19.

The preform 14 has a slightly tapered inner surface 14' in its topmost area thereby forming a  
25 slightly enlarged cavity as shown in Figure 4B which enables the metering tolerance of molten barrier material 6' to be taken up by allowing this to only partially fill the enlarged cavity at 14'. This effect is illustrated at Figure 4C. At position C of  
30 Figure 4A, the displacement rod 18 is pressed down hydraulically and can therefore create a very large flow pressure directly in the molten barrier material 6', this being far greater than that which can be generated by conventional injection mold pumping  
35 devices. The high pressure thus generated permits even flow of molten barrier material 6' in a very

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5 narrow channel formed between displacement rod 18 and  
preform 14. This in turn enables a very thin inner  
layer whereas this would not be possible by  
conventional injection into such a narrow channel,  
10 because the very high pressure needed for inducing  
flow and filling the whole channel would not be  
practicable using injection mold pumping devices.  
Furthermore, since the molten barrier material 6' is  
premeasured to fill the whole channel formed between  
15 the displacement rod 18 and the preform 14, with the  
exception of the partial filling of the enlarged  
cavity at 14', a greater control of the evenness of  
the thin inner layer is possible than that provided by  
conventional injection molding technology, since such  
conventional technology cannot meter the amount of  
material entering the mold.

Finally, when desired, the displacement rod 18  
can be rotated at a predetermined speed for enabling  
better radial flow around the channel formed between  
20 displacement rod 18 and preform 14, also contributing  
to coating evenness. Particularly, since molten  
polymers are generally thixotropic and reduce their  
viscosity with applied shear force, the shear force  
exerted by the rotating displacement rod 18 in the  
25 molten barrier material 6' reduces the viscosity and  
enhances even flow. Additionally, this reduces the  
hydraulic pressure needed to press the displacement  
rod 18 into the preform 14. With certain plastics,  
this shearing action can also enable orientation of  
30 the plastic, enhancing its barrier properties,  
provided the molten barrier material 6' is kept at the  
appropriate temperature during its displacement.

When the displacement of the molten barrier  
material 6' is completed, the preform 14 is reinserted  
35 into the cooling mantel 20 shown at position A of  
Figure 4A and a cooling fluid is switched to flow in

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place of heating fluid in channel 19. The barrier material 6' now solidifies to form an inner layer 22 within preform 14. If the adhesion of the barrier material 6' of the inner layer 22 with the main material of the preform 14 requires an adhesive or a "tie layer", this can be introduced in the same manner as described before. This results in an adhesive layer, not shown, between the material of the preform 14 and the inner layer 22. Depending on the adhesive system used, the need to melt the internal surface of the preform 14, as represented at A, may prove unnecessary. This process can, as before, be implemented as shown in Figure 2 with a plurality of core rods 1 and cavity molds 7 by providing a plurality of heaters 15, depositors 16, and displacement rods 19. Also, a plurality of blow molding positions can be served by providing a multiplicity of heaters 23 or coolers, if needed, in the same position.

The preform 14 including the barrier layer 22 is now finished and can be passed to a conventional container blowing machine. As shown in Figure 5, a conventional blow molding machine includes radiant heater elements 25 which operate to raise the temperature of the preform 14 above a glass transition temperature, so that the material of the preform 14 can be stretch blown into a blow mold cavity, not shown. Conventional heat shields 24 are also used to protect the screw threads if formed of the opening 26 of the preform 14.

However, in contrast to conventional pre-blow-molding heat treatment, because the layer 22 of the barrier material 6' within the preform 14 is very thin, it can be provided with a differential heat treatment, thus enabling the use of an inner layer 22 with a different glass transition temperature than

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preform 14. To enable differential heat treatment, a radiant heater 23 is added to the conventional equipment and introduced as shown in Figure 5 to heat the inside of the preform 14 when the inner layer 22 has a higher glass transition temperature than the main material of the preform 14. Alternatively, when the inner layer 22 has a lower transition temperature than the main material of the preform 14, a cooling tube, not shown, is inserted in place of heater 23 to reduce the thermal stress of the thin inner layer 22 within the preform 14.

Having thus shown and described what is considered to be the preferred methods and respective embodiments for implementing the subject invention, it should be noted that all modifications, alterations and changes coming within the spirit and scope of the invention are herein meant to be included.

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CLAIMS

1           1. A method of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer,  
4 comprising the steps of:  
5           (a) heating a molding core rod;  
6           (b) inserting the core rod into a core rod  
7 receiver;  
8           (c) filling a gap formed between the core rod and  
9 the core rod receiver with a first polymer while being  
10 in a molten state, said first polymer having a  
11 predetermined barrier and/or inertness characteristic  
12 so as to form a thin barrier layer on said core rod;  
13           (d) removing the core rod from the core rod  
14 receiver while the thin barrier layer is still in a  
15 molten state;  
16           (e) inserting the core rod and the thin barrier  
17 layer into an injection cavity mold;  
18           (f) cooling the core rod; and  
19           (g) feeding a second polymer into the injection  
20 mold and flowing said second polymer over the thin  
21 barrier layer while still molten, thereby fabricating  
22 a preform having a thin inner layer of barrier  
23 material.

1           2. The method of claim 1 and additionally  
2 including another step between steps (d) and (e) of  
3 forming a layer of adhesive on said thin barrier  
4 layer.

1           3. The method of claim 2 wherein said another  
2 step of providing an adhesive layer comprises  
3 inserting the core rod with said thin barrier layer  
4 formed thereon into a core rod receiver containing  
5 adhesive material.

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1           4. A method of fabricating a relatively thin.  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer,  
4 comprising the steps of:

5           (a) cooling a molding core rod;

6           (b) cooling a core rod receiver;

7           (c) inserting the core rod into the core rod  
8 receiver and forming a gap therebetween;

9           (d) injecting a first polymer in said gap while  
10 being in a molten state and having predetermined  
11 barrier and/or inertness characteristic so as to form  
12 a thin barrier layer of said first polymer on said  
13 core rod;

14           (e) removing the core rod from the core rod  
15 receiver when the first polymer in the gap solidifies,  
16 thereby providing an external sleeve of said first  
17 polymer on the core rod;

18           (f) heating the core rod and the external sleeve  
19 of said first polymer;

20           (g) inserting the core rod and the external  
21 sleeve into an injection cavity mold; and

22           (h) feeding a second polymer into the injection  
23 cavity mold and flowing the second polymer over the  
24 external sleeve of said first polymer to fabricate a  
25 preform having a thin inner layer of barrier material.

1           5. The method of claim 4 and additionally  
2 including another step between steps (f) and (g) of  
3 forming a layer of adhesive on said sleeve.

1           6. The method of claim 5 wherein said another  
2 step of providing an adhesive layer comprises  
3 inserting the core rod with said thin barrier layer  
4 comprising an external sleeve into a core rod receiver  
5 containing adhesive material.



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1           7. A method of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer,  
4 comprising the steps of:

5           (a) cooling a molding core rod;  
6           (b) cooling a core rod receiver;  
7           (c) inserting the core rod into the core rod  
8 receiver and forming a gap therebetween;

9           (d) injecting a first polymer in said gap while  
10 being in a molten state and having predetermined  
11 barrier and/or inertness characteristic so as to form  
12 a thin barrier layer of said first polymer on said  
13 core rod;

14           (e) removing the core rod from the core rod  
15 receiver when the first polymer in the gap solidifies  
16 thereby, providing an external sleeve of said first  
17 polymer on the core rod;

18           (f) forming a layer of adhesive material on said  
19 external sleeve of said first polymer;

20           (g) inserting the core rod and the external  
21 sleeve into an injection cavity mold; and

22           (h) feeding a second polymer into the injection  
23 cavity mold and flowing the second polymer over the  
24 external sleeve of the first polymer to fabricate a  
25 preform having a thin inner layer of barrier material.

1           8. A method of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer,  
4 comprising the steps of:

5           (a) heating a molding core rod;

6           (b) rotating a coating depositor having a  
7 depositing slot therein around the core rod and  
8 depositing thereon a thin barrier layer of a first  
9 polymer while being in a molten state, said first  
10 polymer having predetermined barrier and/or inertness

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11 characteristic;

12 (c) removing the depositor from the proximity of  
13 the core rod with the thin barrier layer formed  
14 thereon;

15 (d) inserting the core rod in an injection cavity  
16 mold;

17 (d) cooling the core rod; and

18 (e) feeding a second polymer into the injection  
19 mold and flowing the second polymer over the thin  
20 layer of said first polymer while still molten to form  
21 a preform having a thin inner layer of barrier  
22 material.

1 9. The method of claim 8 and additionally  
2 including another step between steps (c) and (d) of  
3 forming a layer of adhesive on said barrier layer.

1 10. The method of claim 9 wherein said step of  
2 forming a layer of adhesive comprises rotating a  
3 depositor containing an adhesive around the barrier  
4 layer to form an adhesive layer.

1 11. A method of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer,  
4 comprising the steps of:

5 (a) inserting a container preform of said second  
6 polymer into a cooling mantle;

7 (b) inserting a radiant heating element inside of  
8 the preform for melting the inner surface of the  
9 preform while keeping the main body of the preform  
10 relatively cool;

11 (c) withdrawing the preform from the cooling  
12 mantle;

13 (d) placing a depositor of first polymer adjacent  
14 the preform and injecting a predetermined amount of

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15 first polymer while in a molten state, and having  
16 predetermined barrier and/or inertness characteristics  
17 into the preform;

18 (e) inserting means into the preform for  
19 displacing the molten first polymer and evenly  
20 spreading the first polymer inside the preform to form  
21 an inner layer therein; and

22 (f) reinserting the preform into the cooling  
23 mantle and cooling the spreaded first polymer until it  
24 solidifies and forms an inner layer within the  
25 preform.

1 12. A method as defined by claim 11 and  
2 additionally including the step of heating the means  
3 for displacing to enhance the spreading of the first  
4 polymer inside the preform following step (e).

1 13. The method of claim 11 and additionally  
2 including another step between steps (c) and (d) of  
3 forming a layer of adhesive on the inside of said  
4 preform.

1 14. The method of claim 11 and additionally  
2 including the step of cooling the means for displacing  
3 for reducing the thermal stress of said inner layer.

1 15. The method of claim 11 and additionally  
2 including another step following step (3) of rotating  
3 said means for displacing and evenly spreading the  
4 first polymer.

1 16. The method of claim 11 and additionally  
2 including a step (g) of inserting heating means in the  
3 preform for reheating the inner layer to facilitate a  
4 subsequent blow molding of the inner layer.

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1           17. The method of claim 11 and additionally  
2 including a step (g) of inserting cooling means in the  
3 preform for further cooling the inner layer to reduce  
4 thermal stress in the inner layer.

1           18. A system of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer,  
4 comprising:

5           (a) molding core rod and a core rod receiver;

6           (b) means for heating the molding core rod and  
7 for inserting the core rod into the core rod receiver;

8           (c) means for filling a gap formed between the  
9 core rod and the core rod receiver with a first  
10 polymer while being in a molten state, said first  
11 polymer having a predetermined barrier and/or  
12 inertness characteristic so as to form a thin barrier  
13 layer on said core rod;

14           (d) means for removing the core rod from the  
15 core rod receiver while the thin barrier layer is  
16 still in a molten state;

17           (e) an injection cavity mold;

18           (f) means for inserting the core rod and the thin  
19 barrier layer into the injection cavity mold and  
20 cooling the core rod; and

21           (g) means for feeding a second polymer into the  
22 injection mold and flowing said second polymer over  
23 the thin barrier layer while still molten, thereby  
24 fabricating a preform having a thin inner layer of  
25 barrier material.

1           19. The system of claim 18 and additionally  
2 including means for forming a layer of adhesive on  
3 said thin barrier layer prior to flowing said second  
4 polymer over the barrier layer.

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1        20. A system of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer,  
4 comprising:

- 5        (a) a molding core rod and a core rod receiver;  
6        (b) means for cooling the core rod receiver;  
7        (c) means for inserting the core rod into the  
8 core rod receiver and forming a gap therebetween;  
9        (d) means for injecting a first polymer in said  
10 gap while being in a molten state and having  
11 predetermined barrier and/or inertness characteristic  
12 so as to form a thin barrier layer of said first  
13 polymer on said core rod and thereafter removing the  
14 core rod from the core rod receiver when the first  
15 polymer in the gap solidifies, providing thereby an  
16 external sleeve of said first polymer on the core rod;  
17        (e) means for heating the core rod and the  
18 external sleeve of said first polymer;  
19        (f) an injection cavity mold;  
20        (g) means for inserting the core rod and the  
21 external sleeve into the injection cavity mold; and  
22        (h) means for feeding a second polymer into the  
23 injection cavity mold and flowing the second polymer  
24 over the external sleeve of said first polymer to  
25 fabricate a preform having a thin inner layer of  
26 barrier material.

1        21. The system of claim 20 and additionally  
2 including means for forming a layer of adhesive on  
3 said sleeve.

1        22. A system of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer:

- 4        (a) a molding core rod and a core rod receiver;  
5        (b) means for cooling the molding core rod and

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6 the core rod receiver;

7 (c) means for inserting the core rod into the  
8 core rod receiver and forming a gap therebetween;

9 (d) means for injecting a first polymer in said  
10 gap while being in a molten state and having  
11 predetermined barrier and/or inertness characteristic  
12 so as to form a thin barrier layer of said first  
13 polymer on said core rod;

14 (e) means for removing the core rod from the  
15 core rod receiver when the first polymer in the gap  
16 solidifies thereby, providing an external sleeve of  
17 said first polymer on the core rod;

18 (f) means for forming a layer of adhesive  
19 material on said external sleeve of said first  
20 polymer;

21 (g) an injection cavity mold;

22 (h) means for inserting the core rod and the  
23 external sleeve into the injection cavity mold; and

24 (i) means for feeding a second polymer into the  
25 injection cavity mold and flowing the second polymer  
26 over the external sleeve of the first polymer to  
27 fabricate a preform having a thin inner layer of  
28 barrier material.

1 23. A system of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer:

4 (a) a molding core rod;

5 (b) means for heating the molding core rod;

6 (c) a coating depositor having a depositing slot  
7 therein locatable around the core rod and including  
8 means for depositing a thin barrier layer of a first  
9 polymer being in a molten state on said core rod, said  
10 first polymer having predetermined barrier and/or  
11 inertness characteristic;

12 (d) means for removing the depositor from the

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13 proximity of the core rod after the thin barrier layer  
14 is formed thereon;

15 (e) an injection cavity mold;

16 (f) means for inserting the core rod in the  
17 injection cavity mold;

18 (g) means for cooling the core rod; and

19 (h) means for feeding a second polymer into the  
20 injection mold and flowing the second polymer over the  
21 thin layer of said first polymer while still molten to  
22 form a preform having a thin inner layer of barrier  
23 material.

1 24. The system of claim 23 and additionally  
2 including means for forming a layer of adhesive on  
3 said barrier layer.

1 25. A system of fabricating a relatively thin  
2 inner layer of a first polymer within a stretch blown  
3 container preform consisting of a second polymer:

4 (a) a container preform;

5 (b) a cooling mantle;

6 (c) means for inserting the container preform of  
7 said second polymer into the cooling mantle;

8 (d) a radiant heating element insertable inside  
9 of the preform for melting the inner surface of the  
10 preform while keeping the main body of the preform  
11 relatively cool;

12 (e) means for withdrawing the preform from the  
13 cooling mantle;

14 (f) a depositor of a first polymer positionable  
15 adjacent the preform for injecting a predetermined  
16 amount of said polymer in a molten state into the  
17 preform, said first polymer having predetermined  
18 barrier and/or inertness characteristics;

19 (g) means insertable into the preform for  
20 displacing the molten first polymer and evenly

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21 spreading the first polymer inside the preform to form  
22 an inner layer therein; and

23 (h) means for again inserting the preform into  
24 the cooling mantle and cooling the spreaded first  
25 polymer until it solidifies, thereby forming an inner  
26 barrier layer within the preform.

1 26. The system of claim 25 and additionally  
2 including means for heating the displacing means to  
3 enhance the spreading of the first polymer inside the  
4 preform.

1 27. The system of claim 25 and additionally  
2 including means for forming a layer of adhesive on the  
3 inside of said preform prior to receiving said first  
4 polymer.

1 28. The system of claim 25 and additionally  
2 including means for cooling the displacing means for  
3 reducing the thermal stress of said inner layer.

1 29. The system of claim 25 and additionally  
2 including means for rotating said means for displacing  
3 and evenly spreading the first polymer.

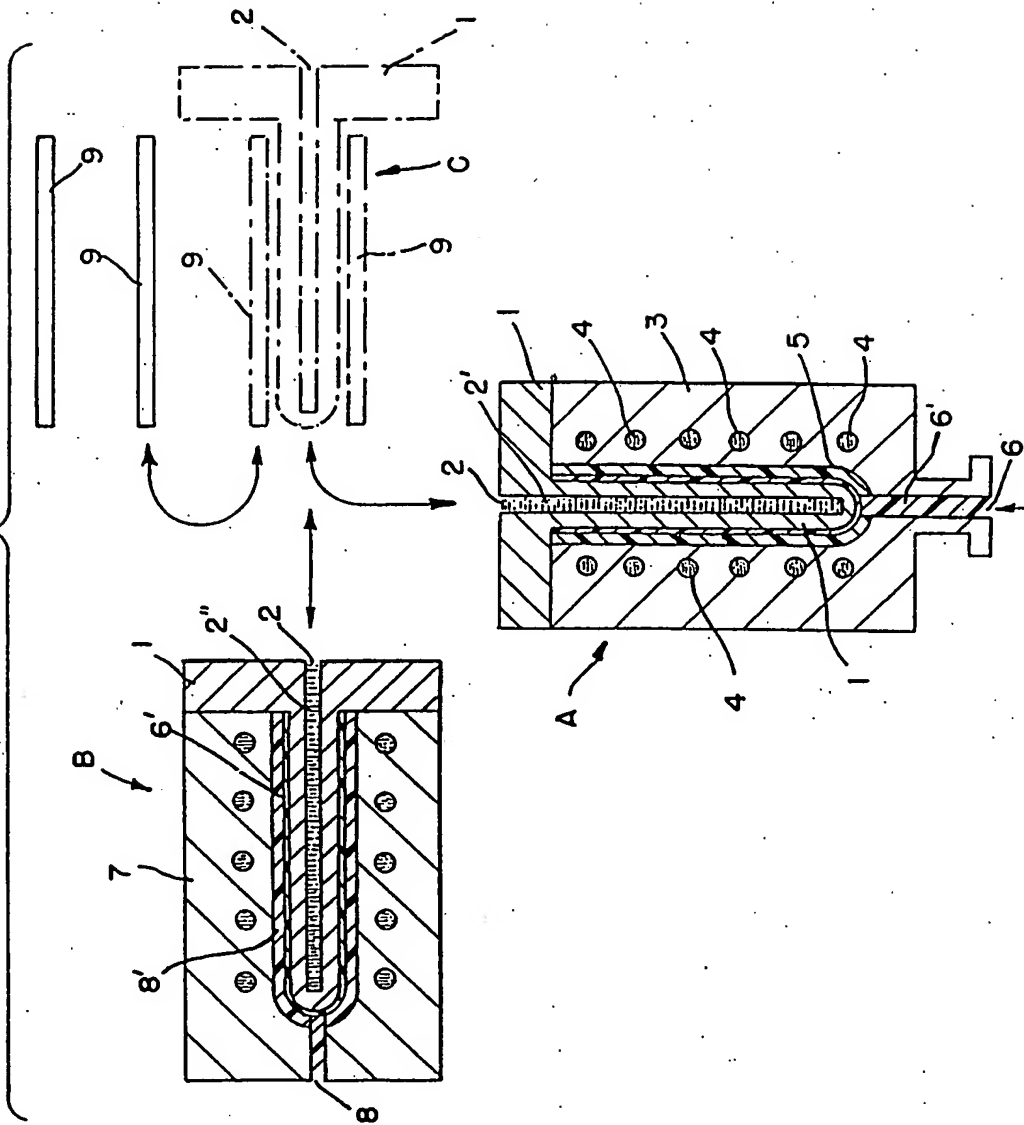
1 30. The system of claim 25 and additionally  
2 including means for reheating the inner layer within  
3 the preform to facilitate a subsequent blow molding of  
4 the inner layer.

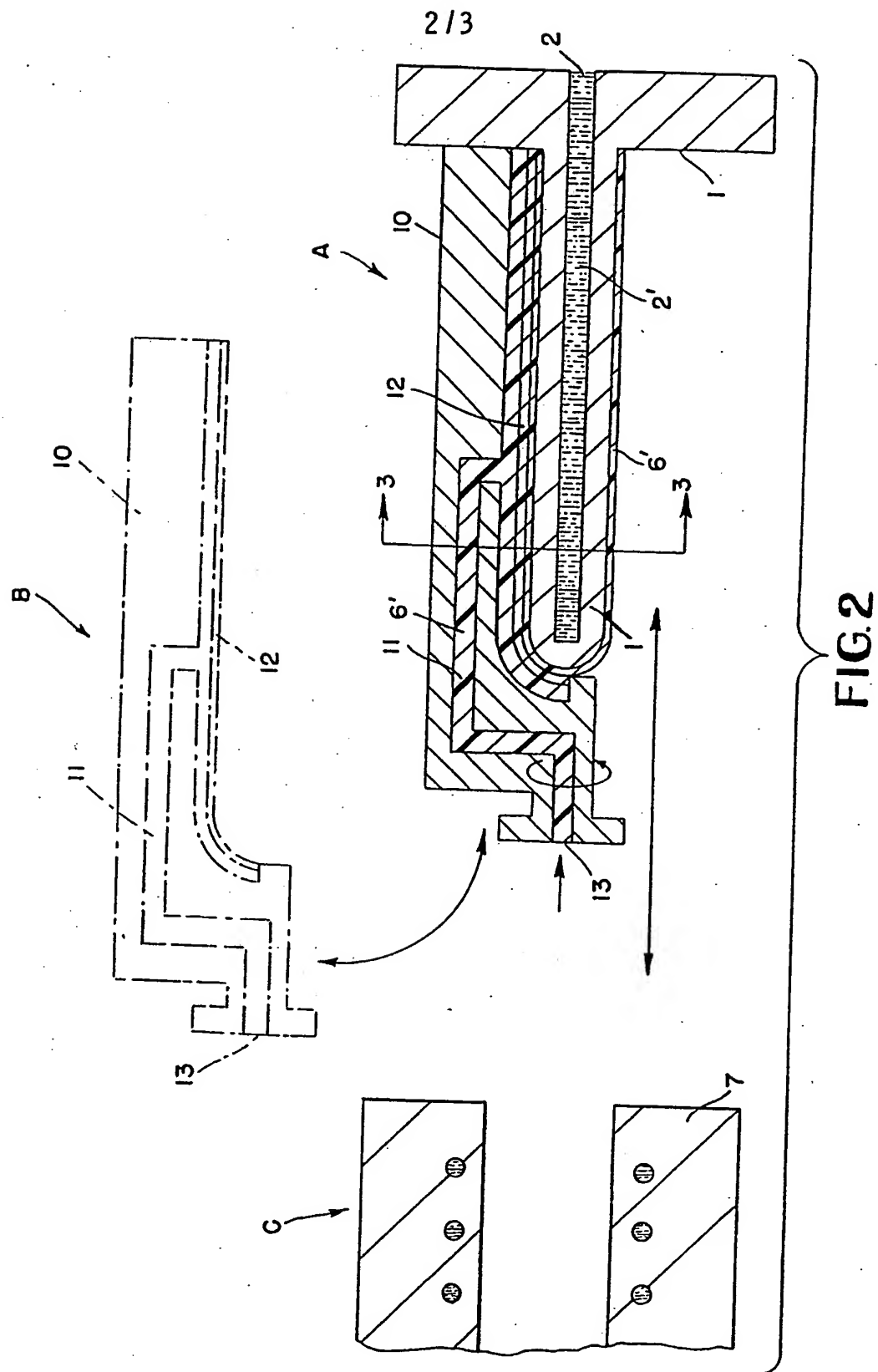
1 31. The system of claim 25 and additionally  
2 including means for further cooling the inner layer in  
3 the preform to reduce the thermal stress therein when  
4 the inner layer has a lower transition temperature  
5 than that of the preform.



1/3

FIG. 1





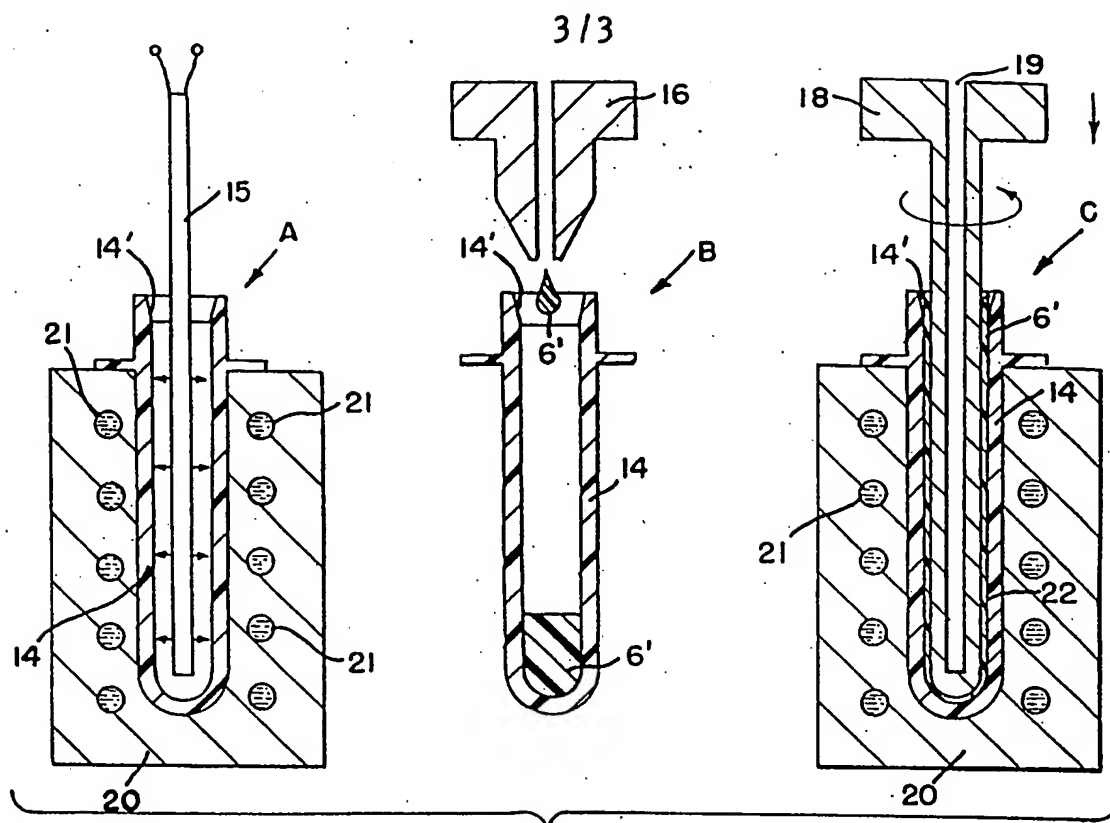


FIG. 4A

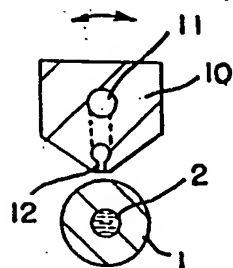
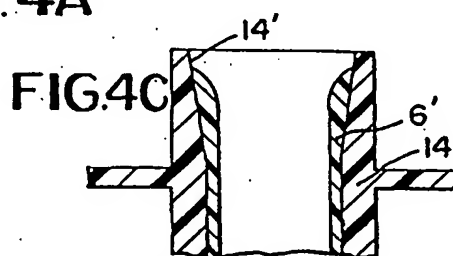
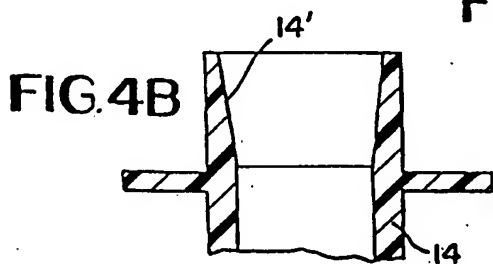


FIG. 3

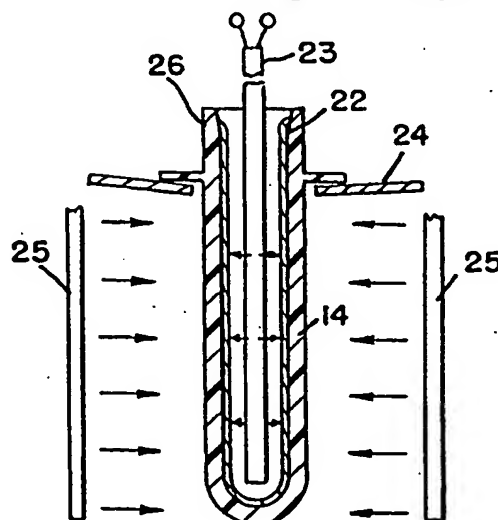


FIG. 5

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/01646

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B29C45/16 B29C49/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	GB,A,2 138 350 (TOYO SEIKAN KAISHA) 24 October 1984 see the whole document ---	1-7, 18-22 8,23
X Y	GB,A,1 482 956 (ILIKON CORP.) 17 August 1977 see the whole document ---	1,4,18, 20 2,5,7, 19,21,22
X	GB,A,2 117 698 (KATASHI AOKI) 19 October 1983 see the whole document ---	1,4,18, 20
X	US,A,3 947 176 (RAINVILLE) 30 March 1976 see the whole document ---	1,4,18, 20
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

1 June 1995

Date of mailing of the international search report

27 / 05 / 95

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Bollen, J

## INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 11 no. 6 (M-551) [2453] ,8 January 1987 & JP,A,61 185417 (MITSUBISHI PLASTICS) 19 August 1986, see abstract ----	1,4,18, 20
X	PATENT ABSTRACTS OF JAPAN vol. 10 no. 51 (M-457) [2108] ,28 February 1986 & JP,A,60 201909 (TOUYOU SEIKAN) 12 October 1985, see abstract ----	1,4,18, 20
Y	AU,D,2 693 871 (IMPERIAL CHEMICAL INDUSTRIES) 28 September 1972 see claims 1,3 ----	2,5,7, 19,21,22
A	PATENT ABSTRACTS OF JAPAN vol. 8 no. 180 (M-318) [1617] ,18 August 1984 & JP,A,59 071832 (TOUYOU SEIKAN) 23 April 1984, see abstract ----	11,25
A	FR,A,2 314 042 (CURETTI) 7 January 1977 see claims 1,3; figures 1-6 ----	11,25
A	DE,A,20 41 514 (HESSER MASCHINENFABRIK AG) 24 February 1972 see the whole document -----	11,25

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/01646

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2138350	24-10-84	JP-C- 1483731	27-02-89
		JP-A- 59158232	07-09-84
		JP-B- 63030132	16-06-88
		SE-B- 463755	21-01-91
		SE-A- 8401063	29-08-84
		US-A- 4517274	14-05-85
		US-A- 4534930	13-08-85
GB-A-1482956	17-08-77	NONE	
GB-A-2117698	19-10-83	JP-A- 58168531	04-10-83
		DE-A- 3311608	06-10-83
		FR-A,B 2524373	07-10-83
US-A-3947176	30-03-76	NONE	
AU-D-2693871	28-09-72	NONE	
FR-A-2314042	07-01-77	CH-A- 595969	28-02-78
		AT-B- 364761	10-11-81
		CA-A- 1077217	13-05-80
		DE-A- 2626342	23-12-76
		GB-A- 1555381	07-11-79
		JP-C- 1316995	15-05-86
		JP-A- 51151773	27-12-76
		JP-B- 60047086	19-10-85
		US-A- 4324541	13-04-82
		US-A- 4243620	06-01-81
DE-A-2041514	24-02-72	NONE	